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SOURCES, WAYS, AND EXTENT OF SOIL POLLUTION

Pollution with Heavy Metals and Metalloids and Ecological Status of Soils in Severobaikal'sk

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Abstract—The content and spatial distribution of 15 heavy metals and metalloids (HMMs) in the upper soil layer (0–10-cm) were determined by data of the geochemical survey in the city of Severobaikal'sk (Republic of Buryatia) in the summer of 2018. The priority pollutants of the topsoil in Severobaikal'sk are Sb, Pb, and W. Soils of the transport, industrial, and single-story residential zones are most strongly polluted. The intensive accumulation is typical for Sb, Pb, and Cu in the first two zones and for Sb, W, Pb, Cd, and Zn in the single-story residential zone. Three associations of HMMs—V–Cr–Co–Ni–Mn; Zn–Cd–Pb; and Sn–Sb–Mo—are inputted from the same sources, and their distribution in the soil cover of the city is similar. The accumulation of HMMs in the upper layer of urban soils is controlled by the content of Fe oxides, C_{org}, pH, and the type of land use, which determines the sources and level of anthropogenic impact on soils. The technogenic impact causes a change in the properties of urban soils, which enhances their ability to fix HMMs. There is no environmental hazard of soil pollution with HMMs for the city, but soils with low and moderately hazardous pollution levels occupy a third of the area of the single-story residential and industrial zones. Formation of several contrasting multielemental anomalies in soils on the bank of the Tyya River and near Lake Baikal is a danger for their waters due to the possibility of the inflow of toxic metals with surface and subsurface runoff.

Keywords: priority pollutants, land use zones, accumulation factors, soil properties, multielemental anomalies

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INTRODUCTION

Anthropogenic impact on urban landscapes results in the formation of a specific environment, in which more than a half of the world population lives now, but which is not always comfortable and favorable for human life [22]. Strong technogenic impact, toxic emissions, solid and liquid wastes of industrial enterprises and motor transport, and municipal waste result in pollution of all components of the urban environment. Soils in cities are subjected to the most considerable transformation and reflect the ecological status of landscapes under the impact of long-term pollution [11]. Ecological and geochemical monitoring of urban soils as the main depositing component in ecosystems is performed in Russia mainly in large cities and megacities. Soils of small and medium industrial cities are studied less comprehensively, so the assessment of their pollution is an important and urgent task.

Heavy metals and metalloids (HMMs) are priority pollutants of the urban environment everywhere [11]. This group includes 58 chemical elements with the atomic numbers from 23 to 92 of the Mendeleev table, from V to U, except for inert gases and halogens [6]. Some HMMs are characterized by high toxicity and carcinogenic activity and thus are considered super-pollutants of the urban environment. Despite the low natural clarke of many HMMs in landscape components, their technogenic anomalies in the upper soil horizons can create environmental risks for man health. For example, migration along food chains and accumulation of Sb, the ecological properties of which are poorly studied, cause damage to the nervous and cardiovascular systems, and inhalation of dust with Sb results in pneumonia, fibrosis, and lung cancer [38]. Poisoning by Cu from food and water causes severe diseases of the gastrointestinal tract, liver, and nervous system, and inhalation of Cu-contaminated air damages respiratory organs [28].

The importance of studying HMMs in urban soils is confirmed by their large extraction volumes in the world, which is accompanied by great emissions, wastes, and sewage of various industrial enterprises. The increase in the technogenic load on the environment is characterized by the technophily index calculated as the ratio of the annual extraction or production of metals to their natural abundances (clarkes) in the lithosphere [19]. For most HMMs, this index increased by two–five times in the second half of the 20th century. The rise in the content of HMMs in the environment during the techno- and urbogenesis causes the metallization of the Earth surface [13].

The aim of this work is to evaluate the content and the danger of soil contamination with HMMs in the city of Severobaikal'sk on the basis of a geochemical survey performed in summer 2018. This city is located on the shore of Lake Baikal, which is a unique object included in the UNESCO World Heritage List. The main pollutants in the snow cover were determined earlier [3]. However, the ecological-geochemical status of urban soils has not been evaluated in detail. The particular goals of the study are as follows:

— to determine the content and spatial distribution pattern of HMMs in the upper soil layer of various land use zones of the city;

— to analyze the main properties of background and urban soils affecting the accumulation of HMMs;

— to reveal technogenic sources of HMMs and factors that favor the formation of anomalies of HMMs in soils;

— to assess the environmental hazard of the pollution of urban soils with HMMs.

STUDY AREA

Severobaikal'sk is located in the Republic of Buryatia, on the northwestern shore of Lake Baikal. The city was founded in 1974 as a base camp for builders of the Buryat section of the Baikal-Amur Mainline and is now a major transport and industrial center.

Environmental conditions. The city is found on the North Baikal Upland. Its geological structure is dominated by Proterozoic metamorphic and intrusive bedrock covered by loose Quaternary sediments represented by silty sands and sandy loams [5]. The surface air in the city is affected by the Asian anticyclone: its cold masses stagnate in depressions in winter, which results in temperature inversions preventing the removal of harmful substances from the atmosphere and favoring their accumulation in soils.

Natural (zonal) soils are assigned to the Baikal piedmont province of raw-humus soils of the high- and mid-mountain Baikal Region [27]. The soil cover pattern of the mountain-taiga zone of the northern Baikal Region is heterogeneous and is mainly related to vertical zoning and slope aspect. Background soils in the region are represented by podburs (Entic Podzols), podzols (Albic Podzols), soddy podzols (Albic Podzols), soddy podburs (Entic Podzols), and raw-humus burozems (Folic Cambisols) [1, 25]. The soils are poorly differentiated, and their profile is thin (about 40 cm in podzols). They are characterized by the coarse texture and high stone content; their water regime is of percolative type, and the soil temperature regime is characterized by the long-term seasonal freezing [26].

In the urban area, native soils are considerably transformed; some of them have lost the features of initial zonal soils. The nutrient supply of plants is decreased, mineralization of dead residues is slowed down, the humus status is changed, and the content of toxic elements is increased [18]. The top layer of urban soils is formed by mixing, addition, burial, or contamination of urbic material. Such soils are assigned to the group of urban soils—urbanozems—with one or more UR (urbic) horizons composed of a specific silty-humus substrate of different thickness and quality with an admixture of construction and household waste [8].

Land use zoning of the area. The structure of land use in the city plays the leading role in the formation of technogenic anomalies of HMMs in soils. In this connection, we performed land use zoning of Severobaikal'sk and identified five zones there: industrial, transport, recreational, and single-story and multistory residential zones (Fig. 1). The map of land use zones was compiled on the basis of the Scheme of Modern Use of the Urban Area and interpretation of Google Earth satellite images.

The industrial zone includes a number of operating enterprises located in different parts of the city: tank farm, the Central thermal power plant (TPP) and two district boiler houses, sewage treatment plant, factory of building materials (Zapbamstroimekhanizatsiya complex of enterprises) in the northwest, services for motorists in the northeast (Motor service station, etc.), and largebakery and other enterprises of light and food industries. The transport zone includes large highways (Ust'-Kut—Uoyan, alternate route of the Baikal-Amur mainline, Leningradskii Avenue and Avenue of 60 years of the USSR), medium highways (Rabochaya, Kosmonavtov, Polygrafistov, Studencheskaya streets), and smaller intra-quarter roads. The residential zone is represented by quarters with different housing density and with social, business, cultural, educational, and medical buildings and shops. Most of them are allocated to the city center. The recreational area is formed by city parks and the coastal area of Lake Baikal, a yacht club, beaches, and the embankment. The main part of the city (36%) is occupied by the residential zone, including 26% of private houses and 10% of multistory buildings. It is followed by the recreational (25%), transport (17%), and industrial (22%) zones.

OBJECTS AND METHODS

The upper (0—10 cm) soil layer was sampled using a regular grid pattern with a step of 500—600 m in Severobaikal'sk and the surrounding area according to the European methodology [30]. This is the upper part (UR1) of the urbic horizon: heterogeneous, brownish-gray, and loose fine subangular blocky structure (often structureless) humus-accumulative layer with a large number of anthropogenic inclusions. In the background undisturbed soils, this is the upper part (0—10 cm) of the humus-accumulative horizon. We sampled 47 mixed (in 3—4 replications) soil samples in different land use zones of the city, two mixed

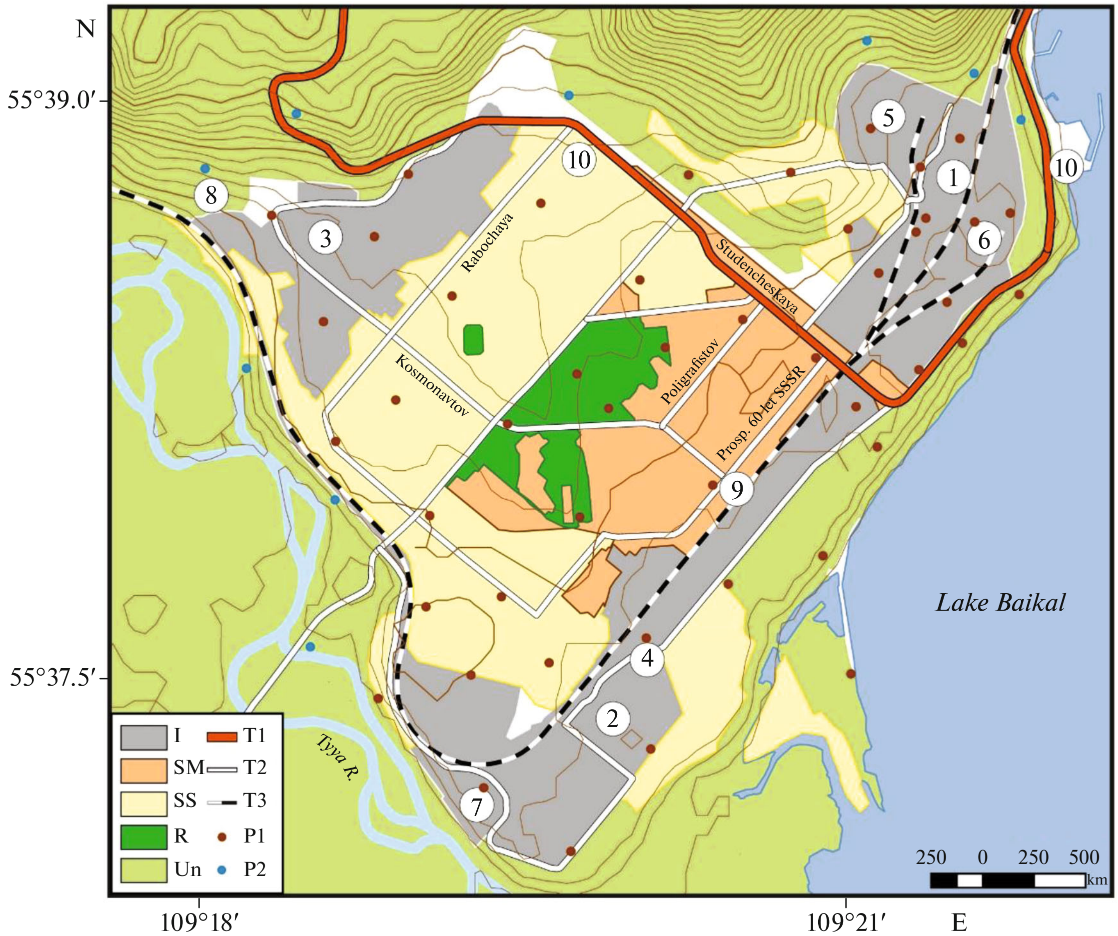

Fig. 1. Map of actual material. Land use zones: I—industrial, SM—multistory residential, SS—single-story residential, R—recreational, and Un—undeveloped and unused areas. T1—large roads, T2—small roads, and T3—railways. Sampling sites from the upper soil layer: P1—urban and P2—background. Numbers on the map indicate the main sources of technogenic impact: (1) central TPP, (2) boiler house no. 11, (3) boiler house no. 12, (4) bakery, (5) oil terminal, (6) locomotive depot, (7) sewage treatment plant, (8) municipal landfill, (9) railway station, and (10) military base.

samples of ash and coal from the area of the Central TPP, and ten samples of background soils.

The total content of HMMs in soils, brown coal, and ash of the TPP was analyzed by the mass spectral (ICP-MS) and the atomic emission (ICP-AES) methods with inductively coupled plasma at the Fedorovskii Research Institute of Mineral Raw Materials on Elan-6100 and Optima-4300 devices (Perkin Elmer, United States). We selected 15 elements assigned to hazard classes I (Zn, As, Pb, Cd), II (Cr, Co, Cu, Mo, Ni, Sb), and III (V, W, Mn), as well as Sn and Bi for detailed analysis.

The main soil properties were determined by conventional methods [16]: actual acidity (pH) in water suspension on an Expert-pH stationary device, the C_{org} content according to Tyurin's method with titrimetric ending, particle-size distribution on an Analyzette 22 laser particle-size analyzer (Germany), and soluble substances-electrolytes by specific electrical conductivity ($EC_{1:5}$) of soil solution on a SevenEasy S30 conductometer (Mettler Toledo) at the Ecological-Geochemical Center of the Department of Geography, Moscow State University.

The analytical data were grouped by the land use zones and processed by statistical methods in the MS Excel and Statistica 10 software packages. The coefficients of accumulation $Kc = Cur/Cb$ and dispersal $Kd = Cb/Cur$ (where Cur and Cb are concentrations of HMMs in urban and background soils, respectively) were calculated for the upper layer of urban soils relative to background analogues. The total soil contamination with HMMs was estimated by the index $Zc = \Sigma Kc - (n - 1)$ with the account of n elements with $Kc > 1$. The Zc index was specified into five gradations: <16—low, non—hazardous; 16–32—medium, moderately dangerous; 32–64—high, dangerous; 64–128—very high, very dangerous; and >128—maximal, extremely dangerous pollution [7, 12]. Regional features of background soils were determined by calcu-

Table 1. The mean content of heavy metals and metalloids in coal and ash of the Central Thermal Power Plant of Severobaikal'sk in comparison with their world clarkes [28]

Element	Coal	Coal clarke	KK_{coal}	Ash	Ash clarke	KK_{ash}	Calculated ash, mg/kg	Kv*
	mg/kg			mg/kg				
Sr	337.6	110	3.07	682.0	740	0.92	5627	8.25
Ba	353.5	150	2.36	748.6	920	0.81	5892	7.87
Mn	108.4	100	1.08	1316	550	2.4	1807	1.37
Ni	12.1	13	0.93	79.1	76	1.04	201.7	2.55
Zn	18.7	23	0.81	47.8	140	0.34	311.7	6.52
Co	2.88	5.1	0.56	21.8	32	0.68	48.0	2.20
Sn	0.51	1.1	0.46	0.73	6.4	0.11	8.5	11.64
Pb	3.31	7.8	0.42	3.42	47	0.07	55.2	16.13
Cr	5.72	16	0.36	26.8	100	0.27	95.3	3.56
V	8.71	25	0.35	48.8	155	0.31	145.2	2.97
Cu	4.78	16	0.30	17.7	92	0.19	79.7	4.50
Cd	0.05	0.22	0.23	0.1	1.2	0.08	0.8	8.33
W	0.2	1.1	0.18	0.61	6.9	0.09	3.3	5.46
Sb	0.1	0.92	0.11	0.27	6.3	0.04	1.7	6.17
Mo	0.22	2.2	0.10	1.57	14	0.11	3.7	2.34
Bi	0.075	0.97	0.08	0.09	5.9	0.02	1.3	13.9
As	0.28	8.3	0.03	2.44	47	0.05	4.7	1.91

* Kv is the volatility coefficient equal to the ratio of the calculated and actual concentration of the element

lated clarkes of concentration $CC = Cb/C$ (at $C < Cb$) or of dispersal $CD = C/Cb$ (if $C > Cb$) relative to the global mean contents of elements in soils (C) [33]. The concentrations of HMMs in brown coal (Ccoal) and ash (Cash) from the Central TPP were compared with the mean contents of HMMs in the brown coals (Kcoal) and ash (Kash) of the world [28] with the calculation of the concentration coefficients KKcoal = Ccoal/Kcoal and KKash = Cash/Kash.

The ecological hazard of particular HMMs in soils was assessed by calculating the coefficient $Kh = Cur(i)/MPCi$, where $MPCi$ is the MPC (or approximate permissible concentration, APC) of the ith element, mg/kg. The contents of V and Sb were compared with their MPC in soils, and those of Cu, As, Cd, Ni, Pb, and Zn with their APC [24]. The soil pollution intensity was mapped according to the values of the Zc index in the ArcGIS 10 package, using graduated symbols.

The Complete linkage algorithm of hierarchical clustering in the Statistica 10 package was used to identify paragenetic associations of HMMs with similar tendencies to accumulation and removal from soils under various landscape-geochemical conditions [23]. The closeness of the correlation between the elements and their statistical significance were assessed by the correlation analysis. The leading factors, affecting the accumulation of HMMs in urban soils, were determined by dendrograms constructed in the Splus package with the use of the method of regression trees [15]. Geochemical maps were compiled in the ArcGIS 10.6.1 package by spline interpolation and land use zoning maps and maps of factual material with sampling points in the Global Mapper 8 and the Google Earth Pro packages.

SOURCES OF HEAVY METALS AND METALLOIDS

Emissions of pollutants into the atmosphere of Severobaikal'sk from stationary sources amounted to 2.6 thousand tons in 2017 [9]. The Central TPP and district boiler houses, using brown coal of the Kansk-Achinsk basin as fuel, are the main suppliers of thermal energy in the city. The used coals are characterized by low content of ash (2–10%), sulfur (0.2–1.2%), and most HMMs [10].

The analysis of chemical composition of Kansk-Achinsk brown coals and ash from the area of the Central TPP of Severobaikal'sk (Table 1) has shown the greatest accumulation of Sr (KKcoal = 3.07), Ba (2.36), and Mn (1.08) in coals and of Mn (KKash = 2.4) and Ni (1.04) in ash relative to the global mean data [28]. The rest HMMs are characterized by low contents. Thus, only Sr, Ba, and Mn are coalphile elements.

The comparison of the actual content of HMMs in ash and the value calculated by the content of HMMs in coals and their mean ash content shows that all the analyzed HMMs are able to condense on the emitted aerosols, migrate with exhaust gases of the TPP, and precipitate on the surface of urban soils. The highest volatility is typical for Pb, Bi, Sn, Cd, Sr, Ba, Zn, Sb, and W, the concentration of which in ash is 16–5.5 times lower as compared to the calculated one.

The objects of transport infrastructure, contributing much to the pollution of the atmosphere and soils of Severobaikal'sk, include the locomotive depot, wagon facilities, coal unloading sites, etc., as well as the road network. Emissions of railway transport enterprises contain dust, soot, carbon oxide, sulfur and nitrogen dioxides, fluoride compounds, hydrocarbons, hydrogen sulfide, HMMs, etc. [35]. High contents of Cd, Cu, Zn, Pb, and As are seen in soils near railways of the Belorusskii station and three railway stations in Moscow [17]. Significant effluents, containing Ni, Cr, Cu, Cd, Cl, Pb, Sb, and Zn, are formed, when washing trains in locomotive depot [21].

The impact of motor transport is caused by exhaust gases, containing Pb, Cu, and Sr; by leaks of engine oil with Zn, Pb, Cu, Sb, and Mo; and by abrasion of tires (Cd, Zn, Pb, Co, Ni, Cr, Cu, and Sb), brake pads (Cu, Sb, Zn, and Pb), and roadway (Ag, Zn, As, W, Cr, V, and Co) [14]. High levels of W and Zn are related to quick wear of tires and brake pads during non-uniform movement [29]. Studies in the east of Moscow have shown that all components of the urban environment accumulate Sb, W, and Sn, and fine fractions are additionally enriched with Cd, Zn, Cu, Pb, Mo, and Bi, on large roads in particular [34]. Sb and Pb are often used to indicate the abrasion of brake pads and discs [31, 32, 37], and tire and roadway wear is indicated by Zn, W, Co, and Cd [29, 36].

Industrial facilities—Nizhneangarskstroi, mobile mechanical department, LenBAMstroi, asphalt and concrete plant—can supply a wide range of HMMs to the urban environment [3, 4]. The production of building materials is related to the processing of natural rocks (limestone, clay, sand, granite, etc.) and of artificial substances. Emissions of these industries into the urban atmosphere usually contain Ag, Pb, W, Sb, and Zn [7], as well as Al, As, Be, Cd, Co, Cu, Fe, Hg, Mn, Ni, Tl, and V [30].

Sewage treatment plants produce waste and wastewater enriched with a large spectrum of toxic elements; Al, As, Ca, Cd, Cl, Cr, Cu, Fe, Hg, Mg, Mn, Na, Ni, P, Pb, Sb, Se, and Zn usually enter the soil with effluents [30]. Landfills of household and industrial waste may be the sources of soil pollution in the city: 9600 tons of waste were produced in 2017 [9].

RESULTS AND DISCUSSION

Main properties of background and urban soils. The upper layer of background soils of the Northern Baikal Region is sandy loamy (19% of physical clay (particles <0.01 mm in diameter)) with a neutral medium reaction (mean pH is 6.9), low mineralization of the water extract ($EC_{1:5}$ is 102 μS/cm), and low organic carbon content (C_{org} is 2.8%). The impact of pollution sources on urban soils has resulted in the transformation of their physicochemical properties, which determine the capacity to absorb HMMs (Table 2, Fig. S1).

The particle-size composition of urban soils does not differ from the background, except for industrial and transport zones, where the content of physical clay increases due to the input of fine technogenic particles. These zones are predominated by light loamy soils, and the rest area is occupied by sandy loamy soils.

Technogenic soil alkalization is typical for all land use zones of Severobaikal'sk, except for recreational zone: the mean pH has increased to 7.4 with a maximum of 8.2 in soils of the transport zone (pH on the background is 6.9). The most acid soils (pH 5.0) are allocated to wetlands of the recreational zone in the southeast of the city, and the most alkaline soils (pH 8.2–8.1) are formed in local areas in the northwest and northeast of the city in the multistory residential, industrial, and transport zones. The increase in pH is explained by the input of carbonate dust to urban soils from industrial enterprises, of construction materials in particular, as well as by the use of deicing reagents in winter. Mean pH in soils decreases in the following sequence of the land use zones: multistory residential (7.69) > industrial (7.65) > transport (7.56) > single-story residential (7.33) > recreational (6.79). The first three zones are characterized by a significant alkalizing effect of carbonate construction dust, pH in the residential zone with private houses insignificantly differs from the background, and the mean pH in the recreational zone is practically equal to the background.

Increased mineralization of the water extract relative to the background revealed in urban soils indicates the development of anthropogenic salinization of the upper layer. The range of $EC_{1:5}$ is from 47.8 μS/cm in soils of the recreational zone to 328 μS/cm in the multistory residential zone and averages 129.3 μS/cm. The high mineralization of the water extract is related to the use of deicing reagents in winter, salt waste from industrial facilities, and municipal wastewater. Urban soils are also characterized by an increase in the C_{org} content as compared to background soils (Table 2). Though the mean C_{org} content in urban soils (3%) differs slightly from the background (2.8%), its value in the industrial zone is 4.1%. Increased C_{org} content in soils (15.6%) has been recorded in the northeast of the city and is caused by emissions of ash particles from the TPP, boiler houses, and the railway center (Fig. S1). Another C_{org} maximum is allocated to the recreational zone: a park in the city center.

The content of HMMs in background and urban soils. Relative to the global mean levels of elements in soils [33], the content of most HMMs in the upper layer of background soils of the Northern Baikal

Table 2. Main properties of the upper (0–10-cm) layer of background soils of the Northern Baikal Region and urban soils in the land use zones of Severobaikal'sk

Land use zone (number of samples)	Content of physical clay, %	pH_{water}	$EC_{1:5}$, µS/cm	C_{org}, %
Background (10)	19.1* (14.2–26.0)	6.9 (5.86–7.52)	102 (37.9–159)	2.8 (1.41–6.42)
Single-story residential (9)	19.2 (15.1–24.2)	7.3 (6.94–8.14)	146 (54.3–328)	2.7 (1.18–6.45)
Multistory residential (5)	19.4 (16.2–24.7)	7.7 (7.24–8.18)	131 (99.9–180)	1.7 (0.97–2.58)
Recreational (12)	18.8 (5.8–25.2)	6.8 (4.97–7.75)	121 (47.8–202)	3.0 (1.65–4.70)
Transport (9)	21.6 (9.6–29.1)	7.6 (6.77–8.22)	124 (72.5–158)	2.4 (0.71–4.4)
Industrial (12)	23.4 (16.2–32.2)	7.7 (6.75–8.05)	128 (70.7–190)	4.1 (1.20–15.59)
Mean for the city (47)	20.6 (5.8–32.2)	7.4 (4.97–8.22)	129 (47.8–328)	3.0 (0.71–15.59)

* Mean values; minimal and maximal values are given in parentheses.

Table 3. The mean content of heavy metals and metalloids (mg/kg) in the upper (0–10-cm) layer of background soils in the Northern Baikal Region (in comparison with the global mean content [33]) and of soils of Severobaikal'sk (in comparison with the background soils)

Element	Background soils (number of samples *n* = 10)				Urban soils (*n* = 47)		
	mean content	world clarke [33]	*CC*	*CD*	mean content	*Kc*	*Kd*
Sb	0.27	0.67	–	2.5	0.74	2.7	–
Pb	20.7	27.0	–	1.3	33.9	1.6	–
W	1.12	1.70	–	1.5	1.66	1.5	–
Cu	22.0	38.9	–	1.8	27.9	1.3	–
Cd	0.23	0.41	–	1.8	0.28	1.2	–
Zn	115.0	70.0	1.6	–	125	1.1	–
Sn	3.25	2.50	1.3	–	3.55	1.1	–
Co	16.4	11.3	1.4	–	16.0	–	1.0
Ni	37.9	29.0	1.3	–	37.4	–	1.0
Bi	0.25	0.42	–	1.7	0.22	–	1.1
Cr	78.6	59.5	1.3	–	69.1	–	1.1
V	90.4	129	–	1.4	85.7	–	1.1
Mo	0.78	1.10	–	1.4	0.74	–	1.1
Mn	1166	488	2.4	–	897	–	1.3
As	6.83	3.79	–	1.8	2.13	–	1.8

Dash signifies that the parameter was not calculated.

Region is low. Natural soils are enriched only with Mn (*CC* 2.4) and Zn (*CC* 1.6), which is explained by their biogenic accumulation in the humus horizon. The rest HMMs are dispersed (the *CD* is 2.5–1.5 for Sb, Cu, Cd, As, Bi, and W and is 1.4 for Mo and V) or their contents are close to the background (Pb, Co, Cr, and Sn) (Table 3).

In the upper layer of urban soils three elements—Sb, Pb, and W—are accumulated relative to the local background (the mean *Kc* is 2.6–1.5). The composition and content of pollutants differ significantly in the land use zones (Table S1), which is clearly reflected by geochemical spectra (Fig. 2). These differences are related to different contribution of pollu-

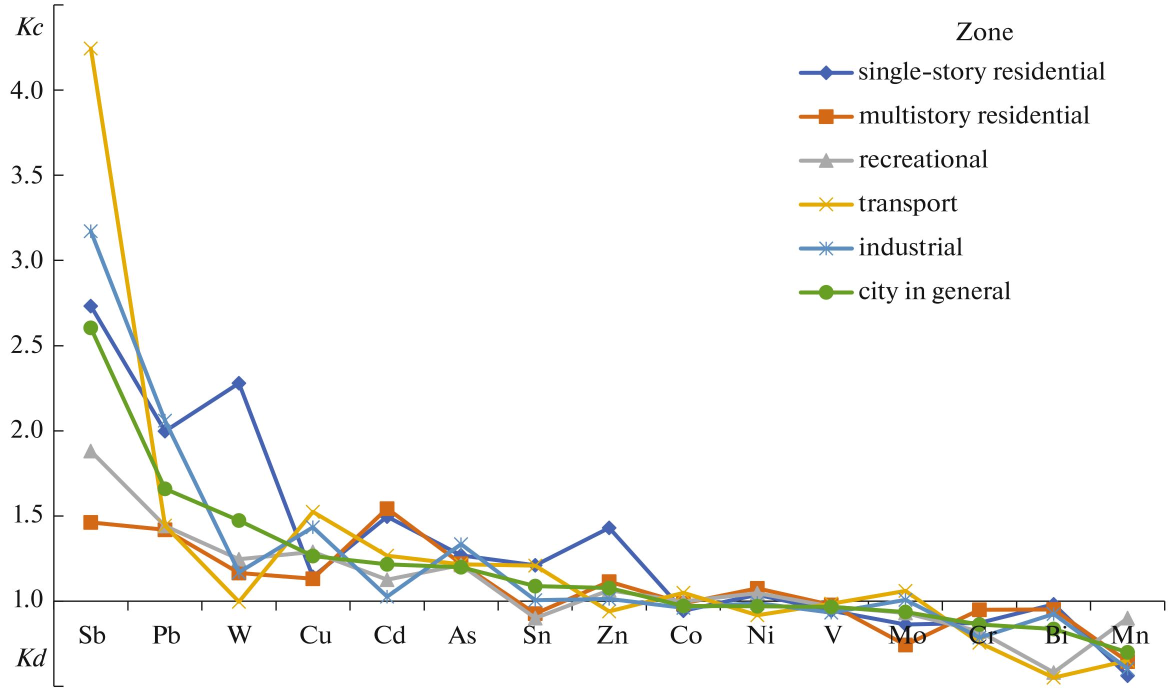

Fig. 2. Geochemical spectra of heavy metals and metalloids in the upper (0–10-cm) soil layer in the land use zones of Severobaikal'sk.

tion sources: emissions from motor vehicles, TPP, boiler houses, railway maintenance enterprises, waste from other industrial enterprises, and household waste. Soils of the transport, industrial, and single-story residential zones are most polluted with HMMs. The first two ones are characterized by the most intensive accumulation of strongly technophile elements: Sb, Pb, and Cu (*Kc* 4.2–1.4) [13]. Soils of the single-story residential zone accumulate Sb, W, Pb, Cd, and Zn (*Kc* 2.7–1.4), and the accumulation of Cd, Sb, and Pb (*Kc* 1.5–1.4) is typical for the multistory residential zone. The input of W, Cd, and Zn to soils of the residential zone is related to municipal waste, emissions, and waste-water discharge. Soils of the recreational zone are the least polluted with HMMs: they are slightly enriched with Sb (*Kc* 1.9), Pb (1.4), and Cu (1.3).

Among HMMs, Sb predominates in soils of the transport (*Kc* 4.2), industrial (3.2), and single-story residential (2.6) zones. The other two accumulation peaks in soils are typical for Pb and W: in the industrial and single-story residential zones for the former (*Kc* 2.1–2.0) and in the residential single-story zone for the latter (2.3). The most intensive dispersion is revealed for Bi in soils of the transport and recreational zones (*Kd* 1.4) and for Mn in the industrial and single-story residential zones (*Kd* 1.4).

Thus, the priority pollutants of soils in Severobaikal'sk include Sb, Pb, and W, and the geochemical specialization of the upper soil horizon is characterized by the following spectrum (lower indices are the *Kc*): $Sb_{2.6}Pb_{1.7}W_{1.5}Cu_{1.3}Cd_{1.2}As_{1.2}Sn_{1.1}Zn_{1.1}Co_{1.0}Ni_{1.0}V_{1.0}Mo_{0.9}Cr_{0.9}Bi_{0.9}Mn_{0.8}$. The revealed set of HMMs in the upper layer of urban soils partially coincides with the data of the State reports On the Status and Protection of the Environment in the Republic of Buryatia of 1991–2003, according to which Cd, Pb, Zn, Hg, F, Mo, and Mn are the main soil pollutants of the Severobaikal'sk industrial complex. The absence of Mo and Mn in our list of priority pollutants may be explained by smaller modern technogenic geochemical load on the area and by the high mobility of these elements at pH < 8, which favors their removal from the upper horizons [20].

Paragenetic associations of HMMs in urban soils. Paragenetic associations of HMMs incoming from the same sources of pollution and characterized by similar tendencies to accumulation and removal under various landscape-geochemical conditions were identified in the upper layer of urban soils, using cluster analysis (Fig. S2). Three associations of HMMs were identified in the upper layer of soils of Severobaikal'sk: V–Cr–Co–Ni ← Mn; Zn–Cd–Pb; and Sn–Sb–Mo. Arsenic, Bi, Cu, and W are not associated with other elements.

The association of V–Cr–Co–Ni ← Mn (with the correlation coefficients between the elements $r = 0.50$–0.81 and $r = 0.50$–0.18 for slighter bonds with Mn) includes siderophile elements, where Ni, Mn, and Co are cationogenic metals, forming a stable bond with anionic V [20]. The formation of this association is not

(a)

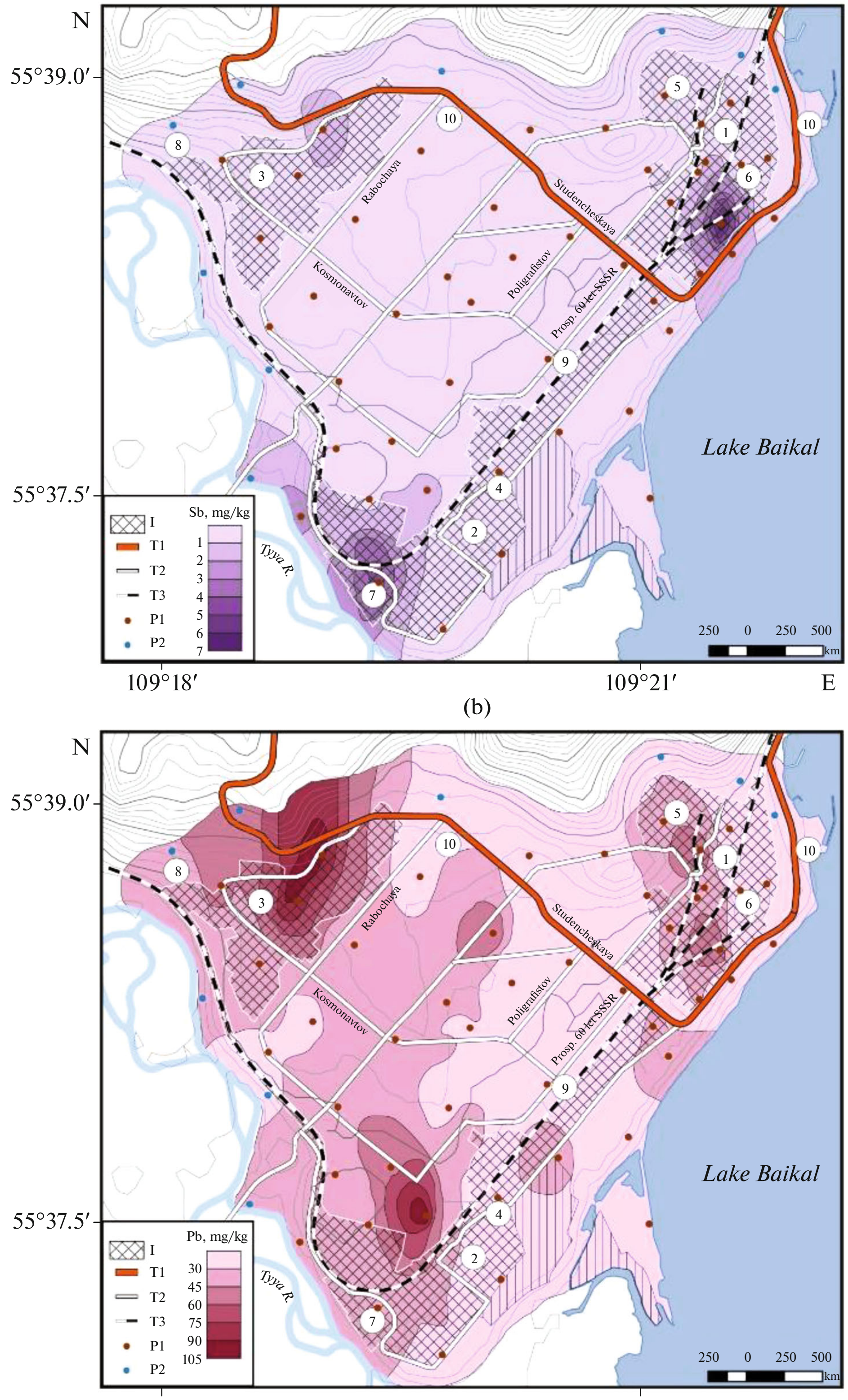

Fig. 3. Distribution of (a) Sb, (b) Pb, and (c) W in the upper (0–10 cm) soil layer in Severobaikal'sk.

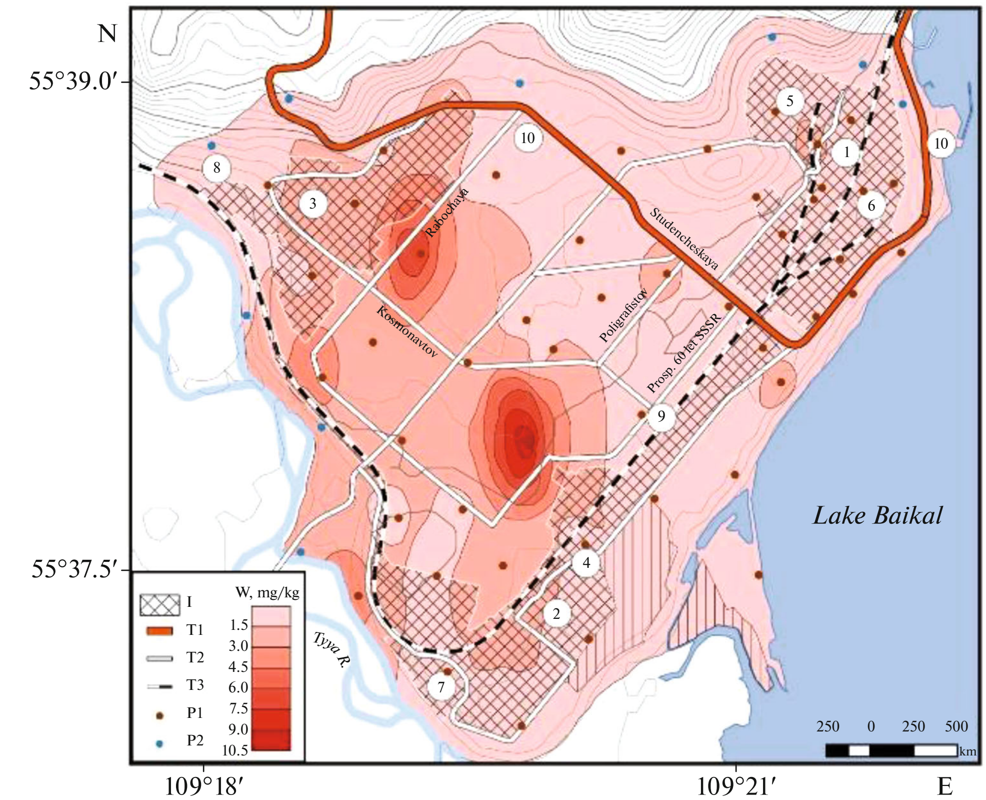

Fig. 3. (Contd.)

related to any particular pollution source; it includes elements mainly of natural origin, the content of which in urban soils is close to the background. Chalcophile Zn–Cd–Pb with strong relations (r = 0.50–0.87) are present in vehicle emissions. The Sb–Sn–Mo association (r = 0.46–0.69) in urban soils includes anionogenic elements.

Technogenic anomalies of HMMs in urban soils. Maps of three priority pollutants Sb, Pb, and W in the upper soil layer have been compiled for the city area (Fig. 3). Several anomalies have been identified for each element; their locations do not coincide with each other, which indicates different pollution sources. Some technogenic anomalies of pollutants, Sb and Pb, in particular, are located not far (up to 500 m) from the edge of Baikal, which may affect the ecological status of lake waters [2].

Technogenic anomalies of Sb in urban soils occupy a relatively small area. There are two large Sb anomalies in the southwest and northeast and one small and low-contrast anomaly in the northwest. The maximum Sb concentrations (5–7.5 mg/kg) in the center of large anomalies exceed the background 17–28 times and the MPC in soils 1.7 times. The formation of the anomalies is related to emissions from the industrial zone and treatment facilities (in the southwest), to the effect of the TPP, locomotive depot, and railway center (in the northeast), and to the emissions from the industrial zone and waste water discharge from the landfill of household waste (in the northwest).

Technogenic anomalies of Pb in the upper soil layer occupy a greater area as compared to Sb. The largest Pb anomaly occupies almost a half of the city area with the maximal Pb content to 75–105 mg/kg, which exceeds 3.5–4.8 times the background and 2.3–3.1 times the APC. The anomaly stretched from north to south is allocated to the industrial and residential zones and is mainly formed under the effect of waste and effluents of motor transport enterprises and vehicles. The second small and slightly contrasting Pb anomaly (to 60 mg/kg) in the northeast is related to the combined impact of industrial enterprises, railway center, and TPP emissions. The third anomaly of the smallest area and the least contrasting (to 30–45 mg/kg) is located on the shore of Baikal and is caused by the lateral migration of Pb from the industrial zone and highway downward the slope to the edge of the lake.

Similar to Pb, the main soil contamination with W is concentrated in the western part of the city, where the element forms a series of rather contrasting anomalies. The W content in their centers increases to 9–10.5 mg/kg, which exceeds the background 8–9 times. Anomalies of W are mainly allocated to the single-story residential zone adjacent to industrial enter-

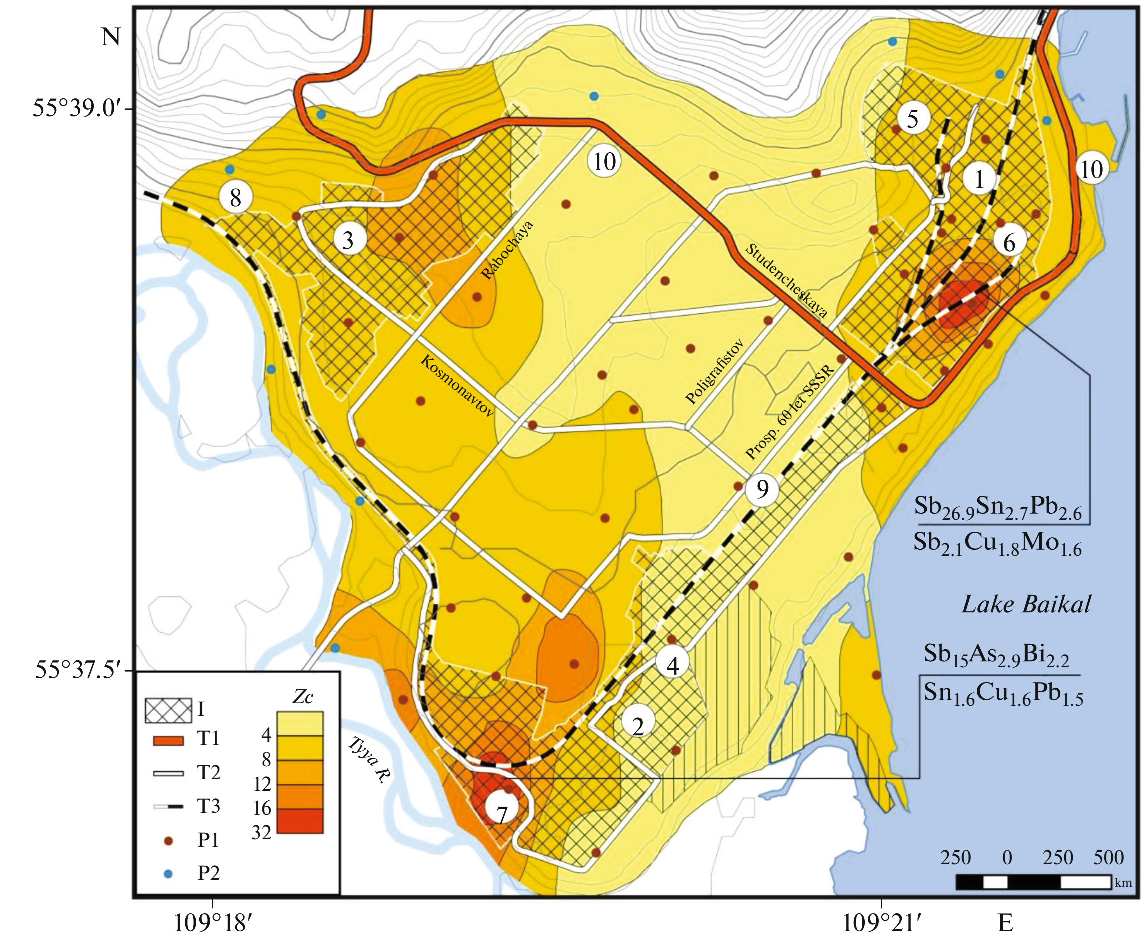

Fig. 4. Total contamination of the upper (0–10-cm) soil layer with heavy metals and metalloids in Severobaikal'sk.

prises. The anomalies were probably formed under the effect of their emissions, where W is used in carbide materials and drilling devices for tunneling. Tungsten is a component of alloy steels, which are widely used for the production of cutting and mining tools [39].

Factors of the accumulation of HMMs in urban soils. A statistical analysis with the construction of dendrograms were performed, using the regression tree method (Fig. S3), to identify the leading factors of the accumulation of priority pollutants in the upper soil layer of Severobaikal'sk. Two groups of factors were taken into account: (1) anthropogenic, the impact of which was characterized by the allocation to a particular land use zone and (2) main soil properties: acid-base conditions (pH); specific electrical conductivity of water extract ($EC_{1:5}$); and the content of organic matter (C_{org}), physical clay, and Fe and Mn oxides. Landscape factors (relief, soil-forming rocks, and vegetation) were not taken into account due to their small variability within the city.

The main distribution factor of Sb—the leading element among HMMs in soils of Severobaikal'sk—is organic matter, the content of which varies in the land use zones of the city. The Sb accumulation is maximal in the least C_{org}-enriched soils (1.3%), which is not typical for natural soils. This is related to the fact that soils in the most polluted areas near the main emission sources of HMMs are strongly transformed and contain minimal amount of organic substances. When the C_{org} content exceeds 1.3%, the Sb accumulation in soils is determined by the amount of Fe oxides: when it is >7.1%, the Sb content increases 2.4 times. At a lower Fe content, acid-base conditions exert a strong effect on Sb accumulation. In the alkaline medium ($pH > 7.9$), the Sb content in soils increases 2.1 times on average.

The accumulation of Pb in urban soils is determined by the land use zone. The multistory residential, recreational, and transport zones are characterized by medium Pb content (28.1 mg/kg), and industrial and single-story residential zones are more intensively polluted (the mean Pb content is 42.0 mg/kg), which testifies to several technogenic sources of Pb in Severobaikal'sk. The increased ($EC_{1:5} > 115$ μS/cm) content of easily soluble salts in soils of the industrial and single-

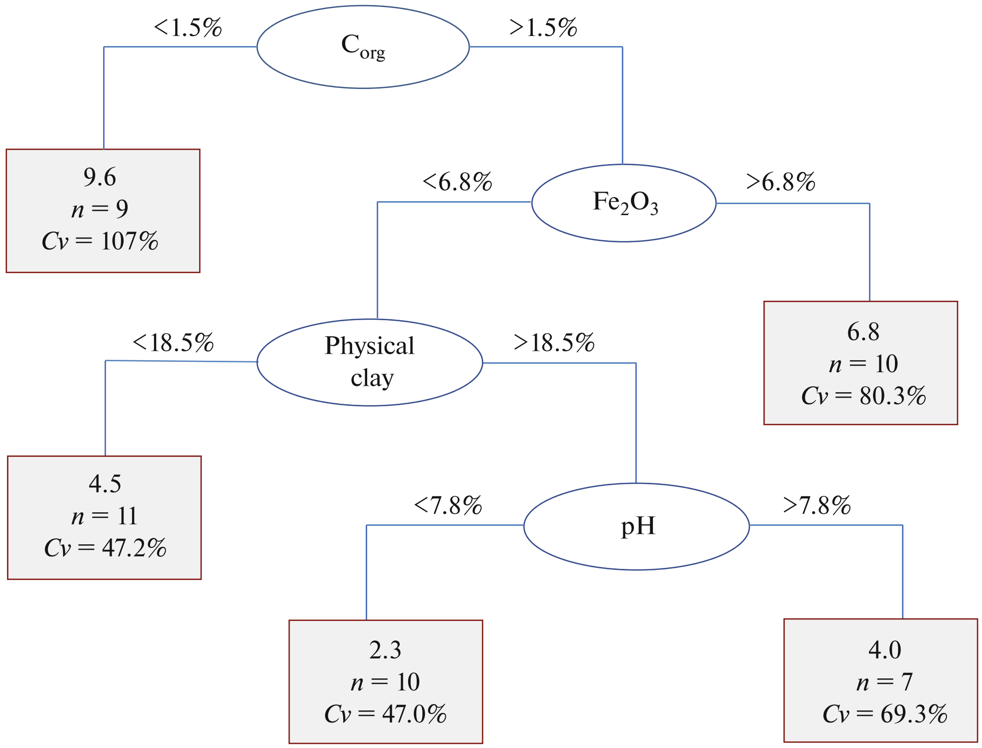

Fig. 5. Factors (in ovals) of accumulation of heavy metals and metalloids in the upper (0–10-cm) soil layer of Severobaikal'sk. The mean total pollution index *Zc*, the variation coefficient *Cv*, and the number of sampling sites *n* are given for terminal nodes (in rectangles).

story residential zones is accompanied by 1.7-time increase in Pb content. Differences in Pb accumulation in the multistory residential, recreational, and transport zones are determined by Fe oxides: in case of their concentrations within 6.4–6.9%, the Pb content increases to 35.8 mg/kg.

The W distribution is related to the particle-size composition of soils: the metal content is maximal (4.3 mg/kg) at 17.6–18.4% of physical clay in soils of the single-story residential zone. In soils with heavier particle-size composition, the W accumulation depends on the medium reaction: its content in the upper soil layer rises 1.3 times at pH > 8. An increased W content (2.2 mg/kg) is also revealed in sandy loamy soils of the industrial and residential zones.

Thus, the most significant factors of Sb, Pb, and W accumulation in soils of Severobaikal'sk include the location in a particular land use zone and soil properties, which determine the capacity of soils to absorb HMMs: the content of physical clay and Fe oxides and pH. The accumulation of Pb significantly increases parallel to the electrical conductivity of water extract. Soil organic matter plays a role of a marker: its low content is allocated to areas with the maximal anthropogenic impact.

Ecological danger of pollution of urban soils with HMMs. The comparison of concentrations of Ni, Si, Zn, As, Cd, Pb with the APC has shown that the greatest ecological danger in the zone of sandy loamy soils is represented by Zn and Ni, the standards of which are exceeded in all the samples studied. The frequency of exceeding the standards for As, Pb, and Cu is also quite high: 58, 46, and 21%, respectively. The APC in light loamy soils is four times higher, because the medium reaction is close to neutral. Therefore, in this part of the city, sanitary and hygienic standards for Ni, Cu, Zn, As, Cd, and Pb were not violated. Single excesses were detected for V (in 8.5% of samples), V + Mn (4.3%), Cd (4.3%), and Sb and Mn (2%).

The environmental hazard of urban soil pollution was also evaluated by the total pollution with HMMs: the *Zc* index, which decreases in the following sequence of the land use zones: single-story residential (*Zc* 7.1) > transport (6.8) > industrial (6.0) > multistory residential (3.6) > recreational (3.3). The mean *Zc* for city soils is 5.4, which enables their assignment to very low polluted. Two large anomalies are revealed as a result of the analysis of the spatial *Zc* distribution in soils of the city (Fig. 4): of moderately dangerous contamination with association $Sb_{15}As_{2.9}Bi_{2.2}Sn_{1.6}Cu_{1.6}Pb_{1.5}$ (*Zc* 20.6) near the treatment facilities in the south and of dangerous pollution with association $Sb_{26.9}Sn_{2.7}Pb_{2.6}Cd_{2.1}Cu_{1.8}Mo_{1.6}$ (*Zc* 33.4) near the locomotive depot in the north.

Soils are practically unpolluted with HMMs (*Zc* < 8) in the most (83%) city area, and their pollution is not dangerous in 10.6% (*Zc* 8–16), moderately dangerous in 4.3% (*Zc* 16–32), and dangerous in 2.1% of the area. The single-story residential and industrial zones are the most polluted: a third of their area is occupied by soils of slightly and moderately dangerous pollution (Fig. S4). Soils of the recreational and multistory residential zones are assigned to practically uncontaminated. These ecological conditions are mainly determined by the age of the development: the industrial and the single-story residential zones exist since the city foundation, while the multistory residential and recreational zones appeared relatively recently.

Differentiation of urban soils by the total pollution with HMMs depends on their properties (Fig. 5). Soils with a low organic matter content (C_{org} < 1.5%) are characterized by the maximal pollution. They are mainly allocated to the multistory residential and transport zones, where they occupy areas with a high anthropogenic load and without vegetation. At C_{org} > 1.5%, the accumulation of pollutants increases parallel to the content of Fe oxides. If it is lower than 6.8%, three groups of soils are distinguished, depending on the particle-size composition and medium reaction. Sandy loamy soils are characterized by increased content of HMMs, which may be explained by the proximity to pollution sources. Accumulation of HMMs in soils of heavier particle-size composition depends on the medium reaction: it is almost two times greater in the alkaline range (pH > 7.8) than at lower pH.

CONCLUSIONS

Among HMMs, three elements—Sb, Pb, and W—are the main pollutants of the upper soil layer in Severobaikal'sk. Their accumulation coefficients *Kc* relative to the background are 2.7, 1.6, and 1.5, respectively. Natural soils are characterized by a low content of most HMMs and are only enriched with Mn (*CC* = 2.4) and Zn (*CC* = 1.6), which is explained by their biogenic accumulation in the humus horizon. Soils of the transport, industrial, and single-story residential zones are the most polluted: there is an intensive accumulation of Sb, Pb, and Cu in the first and second zones and of Sb, W, Pb, Cd, and Zn in the third one.

In soils of the city, HMMs form three associations: V–Cr–Co–Ni ← Mn, Zn–Cd–Pb, and Sn–Sb–Mo; they originate from the same sources and characterized by a similar spatial distribution. The elements that are not associated with others are represented by As, Bi, Cu, and W. Priority pollutants Sb, Pb, and W form several large anomalies of different areas and degree of contrast in soils. The transport zone is most polluted with Sb; Pb dominates in the industrial zone, and W is the priority pollutant in the single-story residential zone. The main sources of soil pollution with HMMs include Central thermal power plant and boiler houses, railway and motor transport, the locomotive depot, factories of construction materials, sewage treatment plant, and landfills.

The main factors of accumulation of HMMs in the upper soil layer are represented by the increased content of Fe oxides and low C_{org} and pH, as well as by the type of land use, which determines the sources and rates of anthropogenic load on soils. Anthropogenic impact has caused the transformation of the main properties of urban soils: alkalization, salinization, changes in the organic matter content, heavier particle-size composition, and related to it increased ability of soils to fix HMMs.

The ecological danger of soil contamination with HMMs for the city in general is not great: 89% of the territory is uncontaminated (*Zc* < 8). The single-story residential and industrial zones are the most polluted: a third of their area is occupied by soils of slight (*Zc* 8–16) and moderately dangerous (*Zc* = 16–32) pollution. The presence of several contrasting multielemental anomalies in soils of these land use zones forms conditions for the migration of toxic metals with surface and subsurface runoff into the Tyya River and to the unique ecosystem of Lake Baikal.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

SUPPLEMENTARY INFORMATION

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